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Effects of multimode laser beam in saturated fluorescence spectroscopy

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Abstract. In laser induced fluorescence spectroscopy, the fluorescence signal depends markedly on the intensity distribution of the laser beam. A theory is developed using the rate equations to calculate quantitatively the intensity of the fluorescence signal when a multimode laser beam is incident in an inhomogeneous absorption medium. A superposition of higher order Gaussian laser beams is found to explain satisfactorily the nature of the experimental curves.

1. Introduction

The use of laser for measuring atomic and molecular species concentration is well established. Any one of the three interactions of radiation with matter namely, scattering, absorption and fluorescence can be monitored for the detection and measurement of pollutants. The detectability limits of scattering method (Raman scattering) are many orders of magnitude larger than those for fluorescence. Daily (1977) has suggested that saturated fluorescence spectroscopy can be used for the detection of low concentration of atoms and molecules in flames and in automobile exhaust. The interaction of matter and intense electromagnetic fields is correctly described only by the density matrix formulation. However, the steady state rate equation can be used if the laser pulse rises slowly compared to collisional rates. Daily (1978) used the rate equations and analysed the effects of a Gaussian laser beam intensity distribution on laser induced atomic fluorescence signals. His analysis could not explain the nature of the experimental curves at very high intensity.

In this paper, an analysis is made using the rate equation formulation by taking into account the inhomogeneous Doppler broadening of the absorption line of the atom.

2. Rate equation formulation

When a gas is excited with monochromatic light, the excited molecules return to the ground state spontaneously by emitting the fluorescent light. Following the procedure of Daily (1978), we can get the expression for the fluorescence signal using the rate equations. For a two level atomic system, the excited atomic density is given by

$$N_2 = \frac{N}{(1+g_1/g_2)}\left[\frac{I_\nu}{I^s+I_\nu}\right] \tag{1}$$

where N is the total number density, I_ν is the light intensity, g_1 and g_2 are the multiplicity factors of the ground and the excited states respectively.

$$I^s = \frac{Q+A_{21}}{B_{12}+B_{21}} \tag{2}$$

I^s is the saturation intensity which depends upon the Einstein coefficients and the collisional rate coefficient The fluorescence signal over a volume V and solid angle Ω is given by

$$I_F = \frac{h\nu A_{21}\Omega}{4\pi}\int_v N_2 dV \tag{3}$$

3. Fluorescence signal calculation

Daily (1978) used Gaussian laser beam intensity distribution in equations (1) and (3) to calculate the fluorescence signal. When a multimode laser beam is incident in an inhomogeneous medium, equation (3) gets modified to :

$$I_F = \frac{h\nu A_{21}\Omega}{4\pi(1+g_1/g_2)}\left[\sum_i n_i \int_v \left[\frac{I\nu_i}{I^s+I\nu_i}\right] dV\right] \tag{4}$$

where ni is the population which comes into interaction with ith mode radiation of intensity $I\nu_i$ and bandwidth $\Delta\nu$. If we assume a Doppler broadened population distribution then,

$$n_i = \frac{N}{1{\cdot}063\Delta\nu\Delta\nu_D}\int_{\nu_i-\frac{\Delta\nu}{2}}^{\nu_i+\frac{\Delta\nu}{2}} \exp\{-[2(\nu-\nu_0)/\Delta\nu_D]^2 \ln 2\} d\nu \tag{5}$$

where

$$\Delta\nu_D = \sqrt{\frac{8\ln 2kT}{M\lambda^2}} \tag{6}$$

M is the atomic mass and k is the Boltzman constant.

For the calculation of the fluorescence signal we consider the set of modes with $q = q_0$, $l = 0$, $p = 0, 1, 2, 3, \ldots$. Then the higher order transverse Gaussian modes may be written in circular polar coordinates in the Gaussian-Laguerre form as

$$I_{poqo} = \frac{\Delta}{\pi\omega^2}[L_p(2r^2/\omega^2]^2\exp(-2r^2/\omega^2). \quad (7)$$

For the laser output, one can write the intensity output as,

$$I = I_0 \exp(-2r^2/\omega^2)[1+a^2|L_1|^2+a^4|L_2|^2+\ldots] \quad (8)$$

where the intensity of the p-th mode varies as $|a|^{2p}$. The values of a lies between 0 to 1. Haug and Dabby (1971) have shown that the values of a can be determined from the laser gain characteristics

If we consider an excitation geometry of a slab of thickness δ, equation (4) becomes

$$I_F = C\left[n_0 \int_0^\infty \frac{I_0 \exp(-2r^2/\omega^2)rdr}{I^s+I_0\exp(-2r^2/\omega^2)} + n_1 \int_0^\infty \frac{a^2 I_0 \exp(-2r^2/\omega^2)|L_1(2r^2/\omega^2)|^2 rdr}{I^s+a^2 I_0 \exp(-2r^2/\omega^2)|L_1(2r^2/\omega^2)|^2} + \ldots\ldots\ldots\right] \quad (9)$$

where

$$C = \frac{h\nu A_{21}\Omega\delta}{2(1+g_1/g^2)} \quad \text{and} \quad L_1(2r^2/\omega^2) = 1-2r^2/\omega^2.$$

In equations only the first two integrals contribute significantly to the signal strength. The first integral can be evaluated as

$$\frac{Cn_0\omega^2}{4}\ln[1+I_0/I^s]$$

and the second integral must be integrated numerically. To explain the experimental curves, the following values are choosen.

$\omega = 1{\cdot}75$ mm; $\Delta\nu_D = 12\times10^{10}$ Hy; $\Delta\nu = 2\times10^{10}$ Hy;

mode separation $= 3\times10^{10}$ Hy.

4. Discussion

Equation (9) is evaluated and is plotted in Figure 1 in semilog coordinates along with the experimental curve of Rodrigo and Measures (1973). If the value of a is chosen to be equal to 0·03, then the theoretical curve is found to follow closely the experimental curve. The theoretical curve due to Gaussian beam is also plotted in the figure. It is found that the Gaussian beam satisfies only the lower part of the experimental curve. When the intensity is comparable with the saturation intensity. the higher order mode does not contribute significantly to the fluorescence signal. But at the very high intensity, the contribution from the higher mode must be taken into account.

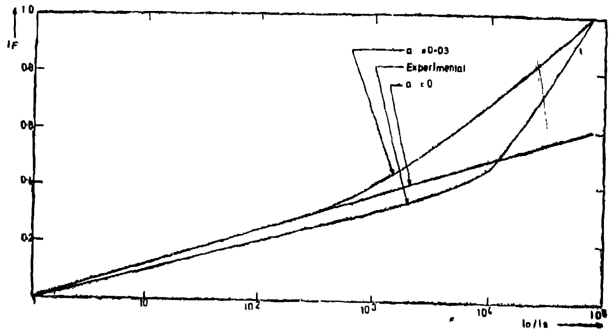

Figure 1. Comparison with the experimental curve of Rodrigo and Measures.

Figure 2 gives the experimental curve of Sharp and Goldwasser (1976). For a value of a equal to 0·25, the theory sives a close fit of the curve. In Figure 3,

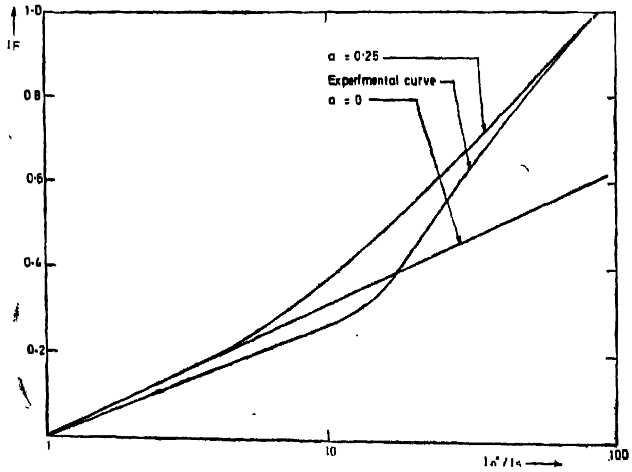

Figure 2. Comparison with the experimental curve of Sharp and Goldwasser.

curves are plotted for various values of a. When a is very small, the curve is almost a straight line. For such small values of a, the nature of the curve can be explained by a Gaussian distribution. For large values of a, higher order mode contributes significantly to the signal strength.

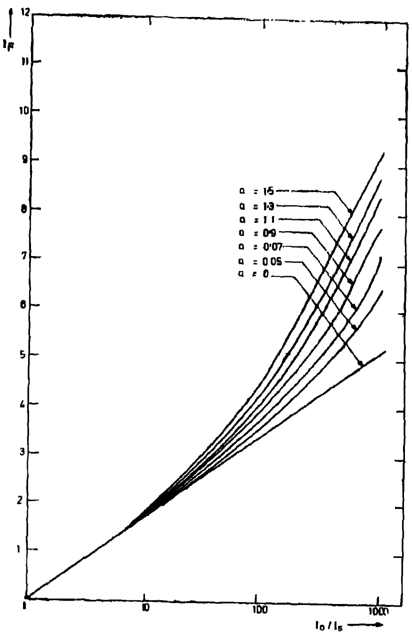

Figure 3. Theoretical curves for various values of a.

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